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## Abstract

Title	Preparation of Composite Electrolytes and Electrodes Having Electrically Conductive Hetero-Interface from Liquid Phase for Electrochemical Devices
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(800 words)

Electrochemical devices that directly convert chemical energy into electric energy are noticeable power sources with high energy conversion efficiency. In particular, polymer electrolyte fuel cells (PEFCs) using proton conductive electrolytes and solar cells using  $\text{TiO}_2$  have attracted much attention because of their potential applications for cogeneration power systems, electric vehicles and mobile electronic devices. On the other hand, recently, there has been a growing interest in the “nanosize” and “interface” effects on fast ionic transfer. Since then, several types of composite electrolytes with heterointerfaces have been demonstrated in order to improve electric conductivity and chemical/thermal stabilities. Layer-by-layer (LBL) assembly is a simple and inexpensive process for multilayer and nanocomposite preparation. Proton-conducting LBL films have attracted attention as a novel thin electrolyte membrane for PEFCs, because thin LBL films can effectively reduce a real resistance of membrane electrolyte.

In this thesis, novel inorganic-organic composite electrolytes and electrodes were prepared by LBL assembly for electrochemical devices. Proton conductive multilayers were deposited on the phenylsilsesquioxane ( $\text{PhSiO}_{3/2}$ ) particles, and then composite electrolytes for PEFCs were prepared from the resultant core-shell particles by pressing. Interfacial proton conductivity of composite electrolyte was discussed on the basis of the relationship with volume fraction of multilayer and estimated by general effective media (GEM) approximation. In addition, multilayered thin film fuel cells (multilayered-TFFCs) employed  $\text{TiO}_2$  photocatalyst as an anodic catalyst were prepared by stepwise depositions of nanoparticles and polyelectrolytes. Electroconductive  $\text{TiO}_2$  composite films were also prepared from the film composed of  $\text{TiO}_2$  (P25) nanoparticles and titania precursor at low temperature and it was utilized as a working electrode of dye sensitized solar cells (DSSCs).

In the first study, thin Nafion films were multilayered on the  $\text{PhSiO}_{3/2}$  particles. Composite electrolytes were prepared from the resultant core-shell particles through a plastic deformation of  $\text{PhSiO}_{3/2}$  particles. An extremely small amount of Nafion was used for the layers. The average thickness of a Nafion layer was estimated to be 2.6 nm from the amount of deposited Nafion and the density. Fenton's test and thermogravimetry revealed that  $\text{PhSiO}_{3/2}$  particles are chemically and thermally stable. The proton conductivity of unmodified  $\text{PhSiO}_{3/2}$  was lower than  $10^{-9}$  S/cm at 80 °C. The monolithic samples prepared using PDDA/Nafion-multilayer-coated  $\text{PhSiO}_{3/2}$  particles showed proton conductivities ~4 orders of magnitude higher than those of samples without multilayers, and their conductivity reached about  $10^{-5}$  S/cm at 80 °C and 80 % relative humidity (R.H.).

Poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) was also multilayered on the size controlled  $\text{PhSiO}_{3/2}$  and the flexible diphenylsiloxane-silica ( $\text{Ph}_2\text{SiO-SiO}_2$ ) particles. An inorganic-organic nanohybrid particle with a two-dimensional chain structure,  $\text{Ph}_2\text{SiO-SiO}_2$ , was prepared by sol-gel process using diphenyldiethoxysilane and tetraethoxysilane. The proton conductivity of the sheets prepared using unmodified  $\text{Ph}_2\text{SiO-SiO}_2$  particles was lower than  $10^{-9}$  S/cm at 80 °C. PAMPS polymer exhibits a high proton conductivity of 0.3 S/cm at 70 °C,

93 %R.H. The equivalent weight (EW: g polymer/mol sulfo groups) of PAMPS is 200 g/mol, which is much smaller than that of Nafion (Nafion<sup>®</sup>117: EW=1100 g/mol). PDDA/PAMPS multilayer-deposited PhSiO<sub>3/2</sub> particles once soften and glued together with plastic deformation at temperatures higher than the glass transition temperature. Sheet-like electrolytes were successfully obtained from the resultant PAMPS-multilayer deposited particles by hot-pressing. Proton conductivity reached about 10<sup>-3</sup>~10<sup>-2</sup> S/cm at 80 °C and 80 % R.H. This is ascribed to the PAMPS layer being concentrated at the particle interfaces, which percolated throughout the monolithic sample.

In the second study, proton conductivity of the percolated PAMPS-multilayer in the composite has been discussed from the mathematical calculation using a percolation model. Proton conductive PAMPS ultrathin film was deposited as a multilayer on the size-controlled PhSiO<sub>3/2</sub> particles via LbL assembly. The composite electrolyte prepared from the PAMPS-multilayer deposited PhSiO<sub>3/2</sub> had a grain boundary composed of the proton conductive multilayer. The interfacial conducting path having a honeycomb structure was percolated in the composite. The volume fraction of the PAMPS-multilayer in the composite was controlled by the change of the PhSiO<sub>3/2</sub> particle diameter. Interfacial proton conductivity of the composite was estimated from the fitting of volume fraction dependence of conductivity using a GEM approximation. The interfacial conductivities of the composite under the conditions of 70 and 95 %R.H. at 80 °C were calculated from the fitting by GEM approximation to be 0.03 and 0.2 S/cm, respectively.

In the third study, the multilayered-TFFCs using anatase TiO<sub>2</sub> as an anodic catalyst were newly prepared by stepwise depositions of nanoparticles and polyelectrolytes. The electrode-membrane assembly (MEA) of the multilayered-TFFC, which had a total thickness of approximately 720 nm, was constructed on a continuously porous glass substrate. The anode and the cathode were separated by the multilayered polymer electrolyte having a thickness of about 350 nm. The multilayered-TFFC was evaluated as direct methanol fuel cell using the photocatalysis for an electric generation. The open circuit voltage was obtained by ultraviolet (UV) irradiation and methanol supply, because electrons were derived from photocurrent and methanol oxidation. The resultant current densities increased with increasing methanol concentration and intensity of UV irradiation. The multilayered-TFFC with 5 mol/L methanol solution showed the maximum power density of 13 μW/cm<sup>2</sup> by UV irradiation of 20 mW/cm<sup>2</sup>. Moreover, the multilayered-TFFC with 1 M ethanol and UV irradiation of 20 mW/cm<sup>2</sup> showed 0.6 V of OCV and 8 μW/cm<sup>2</sup> of maximum power density. The multilayered-TFFCs using anatase TiO<sub>2</sub> are promising for application to photochemical cells, in which low molecular, harmless organic materials are available as fuels.

In addition, a novel DSSC was fabricated using anatase TiO<sub>2</sub> nanocrystals formed by hot-water treatment at 90 °C under ambient pressure. The amount of the precipitated anatase nanocrystals increased with hot-water treatment time. Crystalline TiO<sub>2</sub> composite films were successfully prepared from the film composed of TiO<sub>2</sub> (P25) nanoparticles and titania gel by subsequent hot-water treatment at 90 °C. TiO<sub>2</sub> nanoparticles were interconnected by the sol-gel derived, partially crystallized titania by the continuing hot-water treatment. DSSC using the hot-water treated TiO<sub>2</sub> composite film showed 1.9 mA/cm<sup>2</sup> of short-circuit current density and 0.6 V of open-circuit voltage. The fill factor (ff) and conversion efficiency (η) were 0.63 and 0.71 %, respectively.